



Preparation of magnetic cobalt-based catalyst for hydrogen generation from alkaline NaBH₄ solution

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ABSTRACT

A fast and simple fabrication process, viz. a wet-chemical reduction process, was utilized for preparation of a cobalt-based catalyst to be used for hydrogen generation from alkaline NaBH₄ solution. Characteristics of this cobalt-based catalyst were carried out by using various instruments, such as SEM/EDS, XPS, ICP, VSM, BET and TGA. The surface chemistry of the obtained catalyst is mainly cobalt oxides, not cobalt borides. Ferromagnetic property of the cobalt-based catalyst makes it convenient for being recycled from spent NaBH₄ solution. The rate of hydrogen generation from catalyzed hydrolysis of alkaline NaBH₄ solution was determined as a function of temperature, NaBH₄ concentration, and NaOH concentration in the presence of prepared catalysts. In general, stable generation rate of highly pure hydrogen near 200 mL min⁻¹ g⁻¹ was achieved in 100 mL of 5 wt% NaBH₄ solution containing 5 wt% NaOH solution and 200 mg of Co/IR-120 catalyst, in which no temperature runoff was observed during the course of hydrogen production. The activation energy of NaBH₄ hydrolysis reaction was found at 66.67 kJ mol⁻¹, which was comparable with others reported in the open literatures.

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1. Introduction

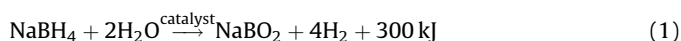
The advancement of technology and the increase of worldwide populations amplify energy consumption significantly, of which most energy comes from fossil origins. Thus, over-consumption of fossil fuels has resulted in climate change and global warming due to the elevated concentration of carbon dioxide in atmosphere. With increasing awareness and necessity of using more efficient and cleaner energy, hydrogen energy has become more and more attractive. However, challenge in hydrogen storage and release in safe and economic ways has been the focus of many researches. For example, steam reforming of natural gas combined with water-gas shift reaction is the most common industrial process to generate hydrogen [1]. However, trace of carbon monoxide contained in produced hydrogen could poison certain catalysts [2], such as platinum, and, hence, causes adverse effects to hydrogen production from the steam-reforming process. Recently, fuels used for reforming have been extended to various short-chained hydrocarbons, such as methanol, ethanol and propane [3–5], and waste plastics [6]. Still, CO levels present in produced gas are of grave concern. Thus, it is imperative to develop a reliable and stable method for continuous supply of pure hydrogen.

Up to now, there are several hydrogen storage methods, such as high pressure tanks, liquefied hydrogen, metal hydrides and chemical hydrides (e.g. KBH₄, NaBH₄, NaH and LiH). In terms of energy cost, high pressure and liquefaction are not preferred due to the fact that extra energy losses must be taken into account in the pressurization and liquefaction process. Moreover, hydrogen content stored in chemical hydrides can be much more than that stored in metal hydrides [7]. Consequently, in order to meet the goals of 6 wt% and 9 wt% hydrogen capacity by 2010 and 2015, respectively, declared by the U.S. Department of Energy (DOE) [8], chemical hydrides are promising materials for hydrogen supply and storage due to their capability in supplying ultrapure H₂ and their larger H₂-storage capacity. Furthermore, some chemical hydrides, such as NaBH₄ and KBH₄, are quite stable in alkaline conditions at ambient temperature. Consequently, proper catalysts are required in hydrogen production from hydrolysis of NaBH₄ and KBH₄.

Among chemical hydrides, sodium borohydride (NaBH₄) is one of the potential compounds for hydrogen storage. Because of its high hydrogen storage capacity, viz. about 10.9 wt%, and its great stability in alkaline solution and non-flammability, it is often applied in controlled generation of hydrogen with specific catalysts. In addition, hydrogen can be generated from NaBH₄ even at 0 °C, which indicates its feasible application in frigid weather. Besides, the main product, sodium metaborate (NaBO₂) after hydrogen production process shown as Eq. (1), can be

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properly recycled [9–12] back to NaBH_4 to lower the cost of using NaBH_4 as hydrogen storage materials.



In general, NaBH_4 solutions are preserved at high pH conditions by adding NaOH to prevent it from self-hydrolysis [13] and maintaining it at chemically stable state. Thus, the rate of hydrogen generation mainly depends on catalysts used.

There are already many reports in the open literature related to hydrogen production from NaBH_4 using different catalysts, which focuses mainly on precious metals, such as ruthenium [14], nickel-boride [15], LiCoO_2 and Co_3O_4 [16], cobalt-boride [17–21] on various supports. Out of these active catalysts, cobalt boride was first reported by Schlesinger et al. [20] in 1953 as an effective catalyst in hydrogen evolution from hydrolysis of sodium borohydride. Such a black cobalt boride catalyst was commonly expressed as Co_2B . However, Schlesinger et al. [20] would rather infer it as a mixture of metallic cobalt, Co , and a cobalt boride, CoB , in constant proportions by weight. Briefly, the cobalt boride catalyst was obtained when CoCl_2 was directly added to sodium borohydride solution [20].

In general, the recycle of used and spent catalysts, is still of grave concern, especially when being applied to supply hydrogen for polymer electrolyte membrane fuel cell (PEMFC) or on-board automobile applications. In our previous study [22], we have developed a fast and simple method to synthesize the polymer template-Ru composite to catalyze the hydrolysis of NaBH_4 for hydrogen generation. High generation rate of hydrogen was thus achieved. Furthermore, lower activation energy in the hydrolysis reaction of NaBH_4 for hydrogen generation was also obtained at about $49.72 \text{ kJ mol}^{-1}$.

It is, therefore, our aim in this study to develop catalysts not only effective in the hydrolysis of NaBH_4 for hydrogen generation, but also easily recycled from spent NaBH_4 solution. A cobalt-based catalyst called Co/IR-120 was successfully synthesized by using a simple chemical wet reduction method, namely a combination of ion-exchange and direct reduction of chelated cobalt ions on polymer supports by sodium borohydride. Different from what cobalt borides, especially Co_2B , were the main chemical on catalysts prepared with procedures described by Schlesinger et al. [20], cobalt oxides were shown with XPS analysis as the dominant species on the surface of Co/IR-120 catalysts.

Compared with fabrication of other noble-metal catalysts, it is cost-effective to make such a cobalt-based catalyst, because of the low material costs of cobalt as well as capability and easiness in scale-up manufacturing of this catalyst. Characteristics of these catalysts, such as magnetism, surface morphology and chemistry, and capability and performance in hydrogen production, were determined accordingly. Because of its magnetic property, these catalysts can be easily recycled with permanent magnets and be reused easily again. With this advantage of easy recycle on used catalysts, durability of Co/IR-120 catalyst in hydrogen generation was also tested. Moreover, factors affecting the rate of hydrogen generation, including NaOH concentrations and NaBH_4 loadings as well as the temperature, were studied and discussed in this report.

2. Experimental

2.1. Materials

Analytical reagent grade sodium borohydride (NaBH_4), borax ($\text{Na}_2\text{B}_4\text{O}_7$), sodium hydroxide (NaOH) (all from Riedel-de Haën), sodium metaborate ($\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$, Alfa Aesar) and cobalt chloride (CoCl_2 , Sigma–Aldrich) were utilized without further purification. A strongly acidic cation exchange resin, Amberlite IR-120 in

hydrogen form (16–45 mesh size), used as catalyst support was purchased from Supelco Chemical Co. (Bellefonte, PA, USA). The properties of Amberlite IR-120 were also given in detail in our previous publication [22]. The active site on Amberlite IR-120 is mainly the $-\text{SO}_3\text{H}$ functional group.

2.2. Preparation of Co/IR-120 catalysts

Preparation of Co/IR-120 catalysts was mainly preceded at ambient conditions. Firstly, weighted amount of Amberlite IR-120 resin beads were placed into Co^{2+} solution to initiate the chelation reaction between resin and cobalt ions. After 1 h of agitation, Amberlite IR-120 chelated with cobalt ion, called Co^{2+} /IR-120, was harvested and washed thoroughly with deionized water to remove any residual Co^{2+} unchelated on the surface of IR-120. Subsequently, the reductive catalysts Co/IR-120 was obtained by reducing the Co^{2+} /IR-120 complexes with suitable amount of NaBH_4 . Finally, the synthesized catalysts, Co/IR-120, were then dried in vacuum at 60°C to get rid of water and hydrogen.

2.3. Hydrogen generation from hydrolysis of NaBH_4

The volume and the rate of hydrogen generated in the presence of Co/IR-120 catalysts were measured by using a water-displacement method, which was described in detail along with its experimental setup in our previous work [22], and also with a continuous mass flowmeter (MFM). The MFM was especially employed to monitor the continuous rate of hydrogen generation from hydrolysis of NaBH_4 in alkaline solutions.

Briefly on determination of H_2 production rate by the method of water-displacement, 15 mL of NaBH_4 solution containing appropriate concentration of NaOH was thermostatically kept in a sealed flask at the preset temperature using thermostatic circulator with a temperature variation within $\pm 0.1^\circ\text{C}$. The onset of the H_2 generation reaction started at 1 min from the moment when a fixed amount, ca. 500 mg, of Co/IR-120 catalysts was introduced into the flask containing NaBH_4 solution. One minute was assumed enough for catalysts to be moistened with NaBH_4 solution. An outlet tube connecting the flask was placed under an inverted water-filled burette, which was situated in a graduated glass column filled with water. The volume of hydrogen released was equal to the volume change of water in the burette.

Similarly, for continuous measurement on H_2 generation rate, 15 mL of NaBH_4 solution with suitable concentration of NaOH was prepared in a funnel equipped with a pressure-equalization at one of the openings of the three-necked round-bottom flask. One of the flask openings was connected to a continuous mass flowmeter (MFM) and the other one to a thermometer. Co/IR-120 catalysts of 500 mg were added into the flask, which was heated to the desired temperature by using thermostatic circulator having good temperature controllability within 0.1°C . The reaction was initiated when NaBH_4 solution was subsequently poured into the flask. The whole H_2 production process was monitored by the MFM.

2.4. Characterization of Co/IR-120 catalysts and spent NaBH_4

The morphology of Co/IR-120 catalyst was identified by using a Jeol JSM-6700F scanning electron microscope (SEM), whereas the elemental compositions on catalyst surface were analyzed with energy dispersive spectra (EDS) and mapping gained from an Oxford INCA-400 spectrometer installed on the SEM.

In addition, the surface composition of these catalysts was monitored by X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS Ultra DLD spectrometer with a monochromatized $\text{Al K}\alpha$ X-ray source (1496.6 eV photons). The core-level signals were obtained at a photoelectron take-off angle of 90° (with respect to the sample

surface), at a constant dwell time of 300 ms, with a pass energy of 40 eV and with the charge neutralizer to minimize surface charging effect. The spectra of elements were curve-fitted by the software XPSPEAK 4.1 with 90% Lorentzian–20% Gaussian peaks to determine the relative atomic concentration of various bondings. After the possible energy shifts caused by charging of the catalyst surface, the required adjustments are made by using an internal reference provided by the C 1s core level of C–C and C–H bonds, whose commonly adopted binding energy is 285.0 eV.

Contents of certain specific elements, namely Co and B, were quantified using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Hewlett Packard 4500). As-prepared catalysts (0.5 g) were first dissolved in 15 mL of 70 wt% nitric acid to leach out substances grown on the surface of IR-120 resin beads. Notably, proper dilution with nitric acid was called prior to ICP-MS analysis.

The specific surface area of Co/IR-120 catalysts and Amberlite IR-120 polymer supports was estimated with a Micromeritics ASAP 2010 Surface Area and Porosimetry analyzer. As-prepared catalysts were first degassed at 100 °C, followed by N₂ adsorption and desorption at 77 K. BET method was used to calculate specific surface area and pore size distribution of these samples.

Thermogravimetric analysis (TGA) was undertaken to estimate the loadings of cobalt on Amberlite IR-120 resin beads using a thermogravimetric analyzer (Perkin Elmer TAC 7/DC), in which air was utilized as both purge gas and working gas at 50 mL min⁻¹. The mass of the analyzed samples was around 20 mg. The temperature program was setup as follows: an isothermal process at 30 °C for 1 min, followed by dynamic heating from 30 °C to 900 °C at a heating rate of 5 °C min⁻¹ and finally held for 1 min at 900 °C. It is noted that all samples were freeze-dried for 24 h to remove any residual water on the surface of Co/IR-120 catalysts prior to TGA analysis.

Magnetic properties of these catalysts were measured with a vibration sample magnetometer (VSM, LakeShore 7404) under an applied magnetic field at room temperature. For convenience, the induced magnetization was reported in emu per gram of catalyst, i.e. emu/(g catalyst).

Chemistry of spent NaBH₄ was analyzed by nuclear magnetic resonance spectroscopy (NMR). ¹¹B NMR spectra were recorded in D₂O at 500 MHz on a Bruker AV-500 NMR spectrometer (Bruker, Rheinstetten, Germany). A saturated solution of boron trifluoride diethyl etherate (BF₃O(C₂H₅)₂, Sigma–Aldrich) was used as an external reference.

3. Results and discussion

3.1. Characterization of Co/IR-120 catalysts

The activity of a catalyst is known to be mostly dependent on its surface properties, such as morphology and surface chemistry. Thus, it is necessary to examine the surface properties of obtained catalysts. Fig. 1 shows as-prepared Co/IR-120 catalysts strongly attracted by permanent magnets with a magnetic strength of ca. 12,000 G, which clearly indicates ferromagnetism present intrinsically in Co/IR-120 catalysts. This ferromagnetic property of Co/IR-120 catalysts certainly gives an advantage on recycle and reuse of catalysts from spent NaBH₄ solutions after hydrogen production and, consequently, leads to a lower operation cost in catalysts. For example, a simple procedure using permanent magnet could easily separate the catalysts from NaBH₄ solutions to stop the hydrogen production when hydrogen is no more required in in-line applications and thus, makes it easier in continuous operation of hydrogen generation from such NaBH₄ system. Certainly, this promotes the safe and reliable production of hydrogen and makes it as a safe portable energy source.



Fig. 1. Photographs of as-prepared Co/IR-120 catalysts placed in a vial with a magnet outside the vial show ferromagnetic behaviors of these catalysts.

Existence of magnetic hysteresis loop on these Co/IR-120 catalysts at room temperature was confirmed with magnetic measurement by a vibration sample magnetometer (VSM) in a range from –11,000 Oe to 11,000 Oe, as shown in Fig. 2. The saturation magnetization (M_S) was estimated at about 4.4 emu/(g catalyst), while remnant magnetization (M_R) and coercivity (H_C) were found to be 0.75 emu/(g catalyst) and 200 Oe, respectively. These magnetic properties certainly indicate soft ferromagnetic nature of the Co/IR-120 catalysts.

Surface morphology of Co/IR-120 catalysts was further examined by an SEM. Fig. 3 shows the SEM micrographs of the IR-120 resin beads as polymer templates and resulted Co/IR-120 catalysts. In general, IR-120 resin beads had relatively smooth surface, while dense flower-shaped structures were observed on Co/IR-120 catalysts (Fig. 3(e) and (f)) after cobalt was reduced on IR-120 by NaBH₄. Dimensions of these flake-like structures were estimated near ca. 300–500 nm (Fig. 3(f)). From the microscopic point of view, the surface of Co/IR-120 was covered with flakes and calyces, in contrast to relatively smooth terrain on IR-120 beads. It

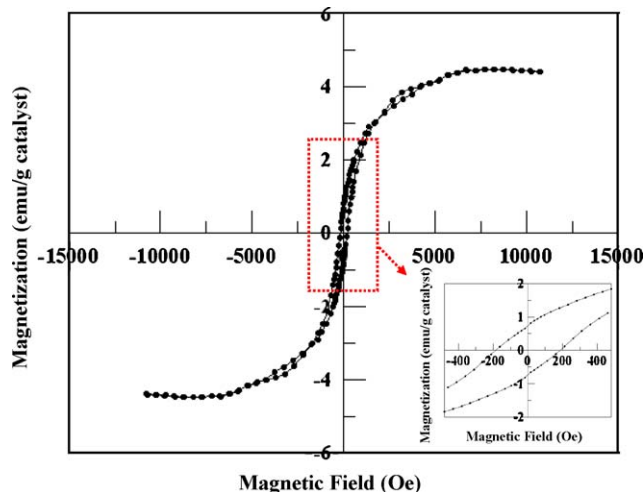


Fig. 2. Magnetic hysteresis loop of Co/IR-120 catalyst measured by a VSM.

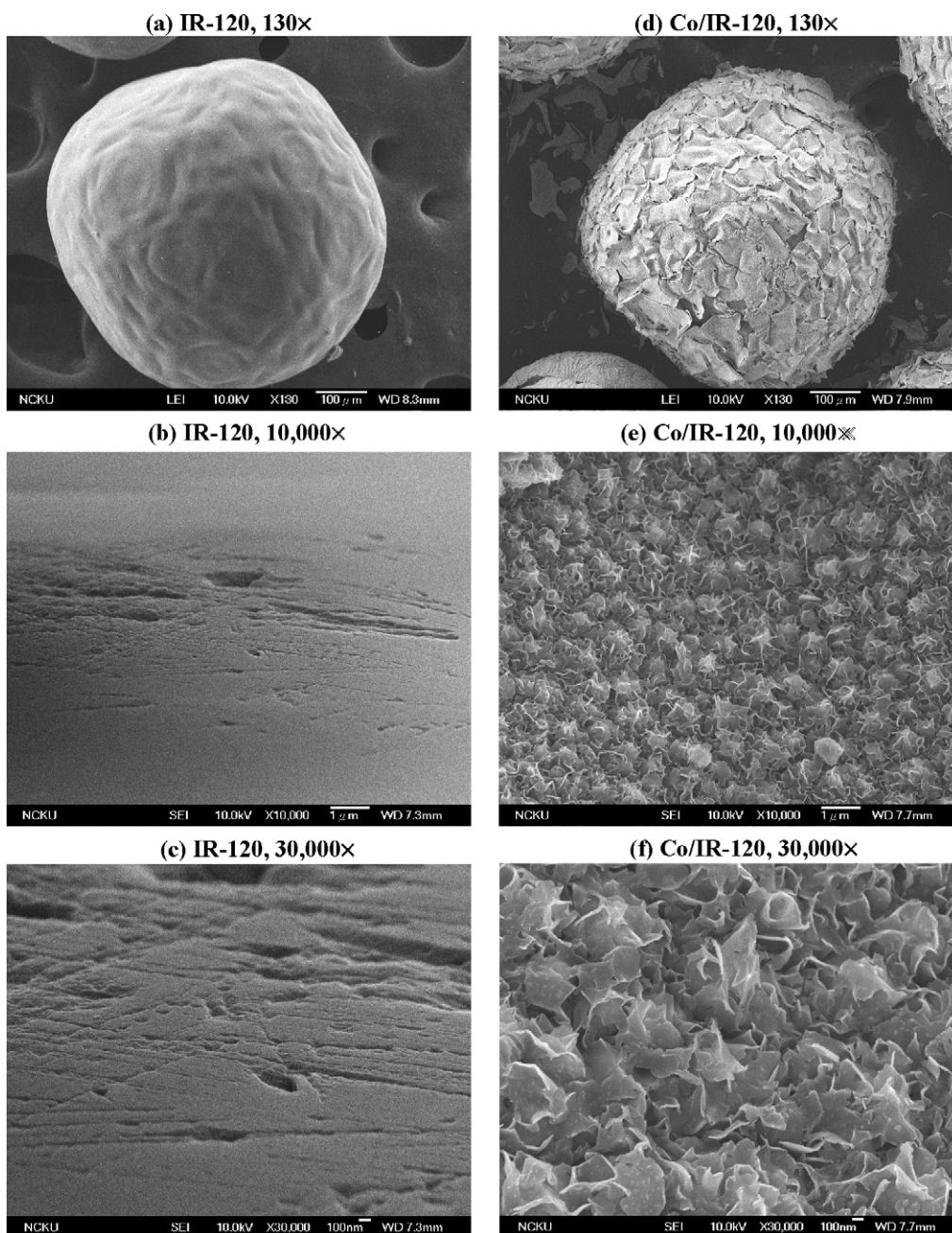


Fig. 3. Scanning electron micrographs of Amberlite IR-120 resin beads: (a) 130×; (b) 10,000×; (c) 30,000×; and Co/IR-120 catalysts (d) 130×; (e) 10,000×; (f) 30,000×.

is, thus, reasonable to infer that flake-like materials were originated from cobalt. Several fissures exist between two adjacent cobalt sheets in lower magnification (130×) as shown in Fig. 3(e). BET measurement disclosed an increasing specific surface area from $0.19 \text{ m}^2 \text{ g}^{-1}$ to $0.47 \text{ m}^2 \text{ g}^{-1}$. The surface area found on these Co/IR-120 catalysts was about two orders of magnitude less than the Co-B catalyst and Co-supported catalysts [17,18], and one order of magnitude less than Co_3O_4 catalyst [16]. One possible cause on the low BET area of Co/IR-120 catalyst was due to its larger particle size near $600 \mu\text{m}$ and lack of nano-porous structures on catalyst surfaces.

However, despite of these low values of specific surface area possessed by Co/IR-120 catalysts, satisfactory production rates of hydrogen from hydrolysis of sodium borohydride solution could be still obtained. The possible reason on hydrogen production being less dependent of BET area of catalysts was

that the hydrolysis reaction mainly took place on the interface of liquid (borohydride solution) and solid (catalytic surface), not on the gas–solid interface on which specific area of catalyst could be one of dominant factors. Specifically speaking, for a liquid entering into a porous structure, the Young–Laplace equation predicts that a capillary pressure greater than the product of the interfacial tension and the total curvature is required. If the reaction requires a liquid with surface tension near 30 mN/m to take place on the inner wall of a mesopore with a radius of 10 nm , an enormous capillary pressure around $6 \times 10^6 \text{ Pa}$, ca. 60 atm , is needed for the reacting liquid to be imbibed into the mesopores, which is very unlikely to happen in this work. Explicitly, even with mesopores on the catalysts, the hydrolysis reaction of NaBH_4 would still mainly occur on the bulk surface of catalysts, and would be affected more possibly by the surface chemistry of catalysts.

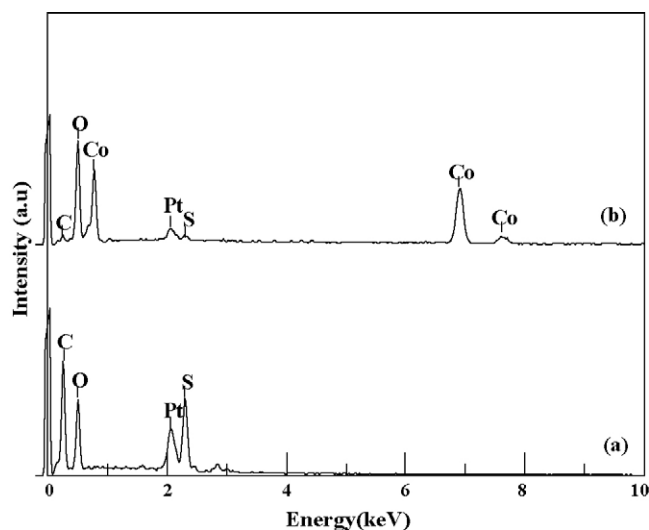


Fig. 4. EDS spectra of (a) Amberlite IR-120 and (b) Co/IR-120 catalysts. Appearance of Pt peaks arose from platinum sputtered on samples prior to SEM/EDS analysis to increase the electric conductivity of these samples.

Surface compositions on IR-120 resin beads and resulted Co/IR-120 catalysts were examined with EDS and XPS, respectively. XPS requires more complicated operation procedures, and reveals composition information and possible bond formation as well as oxidation states of elements only on the first few atomic layers, usually less than 10 nm, from the surface examined. In contrast, EDS gives a larger depth of analysis, which mainly depends on energy of incident electron beams used in SEM/EDS and density of object to be examined. In this work, the depth of analysis of the EDS is estimated at about 190 nm, according to the information supplied by the manufacturer. That is, the EDS analysis really gives an enveloped average of properties in the layer from surface to the depth of analysis.

Fig. 4 exhibits the EDS analyses of IR-120 resin beads and cobalt-loaded IR-120 resin (Co/IR-120). Elements, such as carbon, oxygen and sulfur, were found to be dominative components in original Amberlite IR-120 resin. Notably, the platinum detected should not be originated intrinsically, since specimens must be deposited with a thin layer of platinum to increase their surface conductivity prior to SEM/EDS analysis. After cobalt was reduced on the surface of IR-120, two apparent peaks representing cobalt were detected at around 0.6 keV and 7 keV, shown as curve b on Fig. 4. This undoubtedly corroborated successful deposition of cobalt on the IR-120 resin. Table 1 lists the surface compositions of both IR-120 resin beads and Co/IR-120 catalyst. For example, carbon content dropped from 65.3 at% (or 53.2 wt%) on IR-120 to 12.96 at% (or 4.95 wt%) on Co/IR-120. Simultaneously, Co was not detected on neat IR-120 resin beads, but found around 36.25 at% or 69.43 wt% on Co/IR-120 catalysts. This certainly confirmed that flower-like and calyx structures shown in Fig. 3(d–f) are mostly cobalt.

To realize whether cobalt was uniformly deposited on the Amberlite IR-120 resin beads, elemental distribution on Co/IR-120

catalysts was also conducted with EDS mapping, shown as Fig. 5. The enclosed area in the SEM image of Co/IR-120 catalyst, Fig. 5, corresponds to the selected area where EDS mapping was applied. Distribution of carbon seemed to be more abundant in the trench between calices and coincide closely with that of sulfur on Co/IR-120 catalysts. In addition, cobalt could be found almost everywhere, but quite scarcely in the fissure between calices on the surface of Co/IR-120 catalysts.

Detailed surface compositions and possible bond formation on Co/IR-120 catalysts were identified using XPS analysis. XPS wide scan and core-level spectra of C 1s, O 1s, Co 2p and B 1s of original Co/IR-120 catalysts were exhibited in Fig. 6(a–e) and those of Co 2p and B 1s of used Co/IR-120 catalysts in Fig. 6(f and g). Deconvolution of these peaks was performed using the Xpspeak 4.1 software. Table 2 tabulates the information of possible bonds formed on the surface of original Co/IR-120 catalysts.

It was found that cobalt existed on Co/IR-120 catalyst in metallic and oxidized forms, such as CoO, Co(OH)₂, and Co₃O₄, which were consistent with those found in O 1s core-level spectra. Still, carbon and oxygen were dominant species on the surface of Co/IR-120 catalyst, whereas cobalt only made up 4.3 at% and 13.2 at%, respectively, on fresh and used Co/IR-120 catalysts. Among all cobalt present on Co/IR-120 catalyst, 6.95 at% was in metallic form. Meanwhile, traces of boron and sulfur, less than 0.1 at%, probably arising from the –SO₃H functional groups of Amberlite IR-120 resin were found. Furthermore, with the XPS analysis, boron mostly appeared on Co/IR-120 catalyst as pure boron, BN, B₂O₃ and boric acid (H₃BO₃), of which latter two were also confirmed with their presence in O 1s core-level spectra. The surface concentration of boron was as low as 0.9 at% on fresh Co/IR-120 catalyst and 0.2 at% only on used catalyst, harvested after durability test of catalyst. That is, the atomic ratios of cobalt to boron (Co/B ratio) on fresh and used catalyst were 5.4 and 66, respectively. This finding, especially the Co/B atomic ratio on fresh catalyst, was significantly different from 2, i.e. Co₂B, commonly reported in the literature [17–20].

Indeed, attempts to deconvolute the Co 2p and B 1s core-level spectra obtained from fresh and used Co/IR-120 catalysts with assigned binding energies corresponding to CoB and Co₂B failed to yield any meaningful values. Instead, cobalt oxides and boron oxides, not cobalt borides, were found on Co/IR-120 catalysts regardless before and after hydrolysis reaction of NaBH₄ solutions.

Additionally, contents of cobalt and boron on IR-120 resin beads and Co/IR-120 catalyst were quantified with ICP-MS analysis (Table 3). The atomic ratio of Co/B on Co/IR-120 catalyst was found at 14.8, according to data presented in Table 3. The Co/B atomic ratio obtained from ICP-MS analysis higher than that from XPS-analysis also implied that inner layer of Co/IR-120 catalysts was even richer in cobalt oxides, since the analysis depth of an XPS instrument is only less than 10 nm in contrast to the whole cobalt layer of a micron-scale thickness grown on IR-120 resin beads. Recently, Krishnan et al. [21] reported the use of thin-film CoB catalyst templates for the hydrolysis of NaBH₄ solution for hydrogen generation. Interestingly, the compositions of their electrolessly plated CoB/Ni-foam templates, i.e. Table 2 in Ref. [21], probed by an ICP shows Co/B atomic ratios ranging from 14.1 to 17.4. Namely, B contents in their Co/B catalysts were much less than that required for stoichiometric alloy formation (CoB, Co₂B or Co₃B) [21]. Briefly speaking, both findings in their work [21] and our work were quite consistent.

Though it may still be impossible to rule out the possibility of formation of trace CoB at a level beyond XPS detection on active cobalt catalysts in this work, findings in this work certainly indicate that our preparation method yields active cobalt catalysts with surface chemistry vastly different from previously known catalysts prepared by Schlesinger's method [20].

Table 1

Surface compositions present in Amberlite IR-120 resin and Co/IR-120 catalyst analyzed by EDS.

Elements	Amberlite IR-120 resin		Co/IR-120 catalyst	
	wt%	at%	wt%	at%
C	53.17	65.30	4.95	12.96
O	29.49	26.26	25.52	49.91
S	19.34	9.44	1.10	1.07
Co	0	0	69.43	36.25

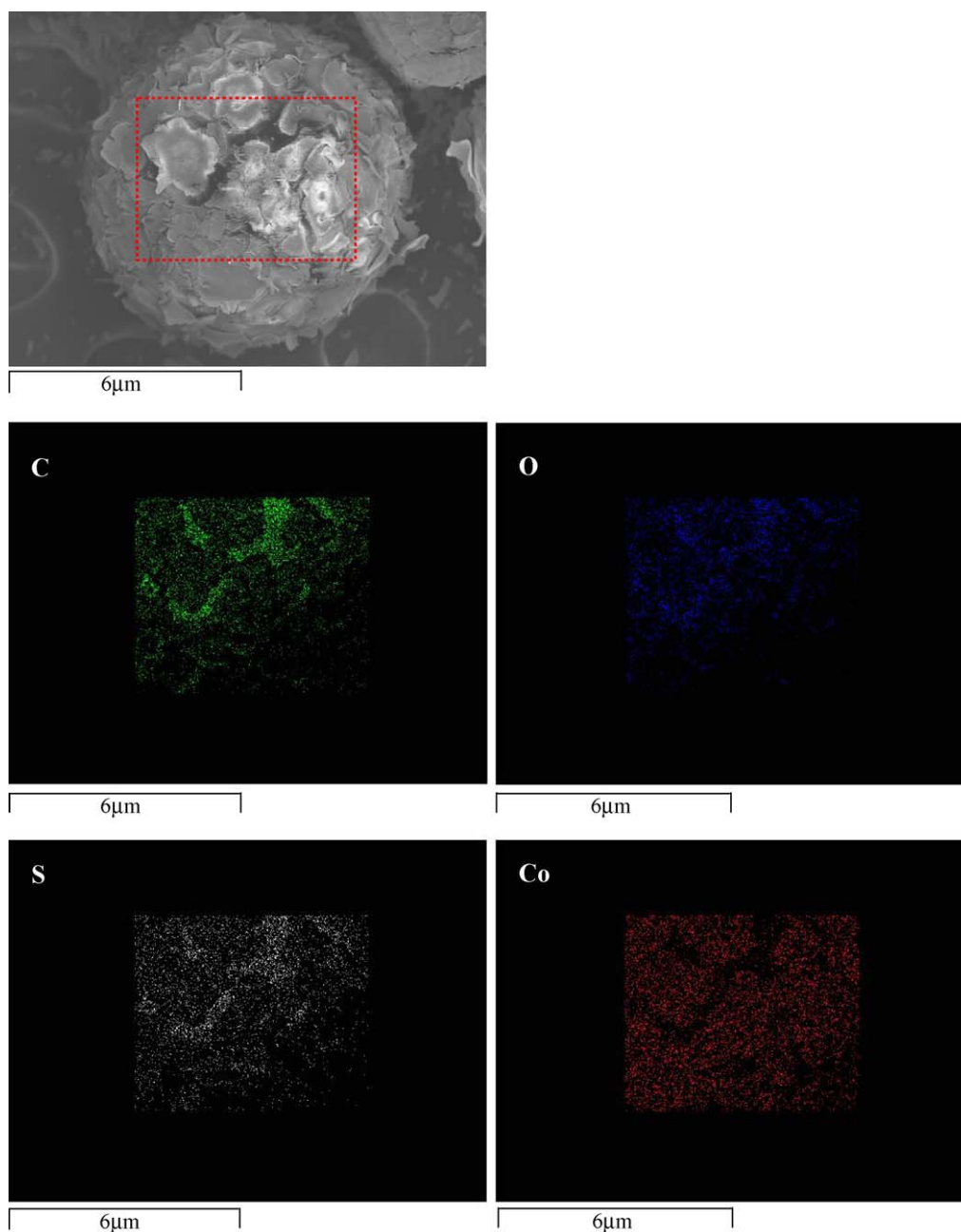
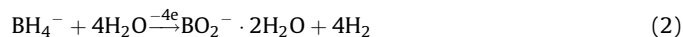


Fig. 5. SEM micrograph of Co/IR catalyst and EDS mapping of Co/IR catalyst showing the elemental distribution of C, O, S and Co.

With the surface chemistry on Co/IR-120 resin revealed by the XPS analysis, a possible mechanism was proposed. Since the reduction of cobalt chelated on resin was performed under slight acidic condition, each borohydride anion would undergo oxidation of four-electron transfer to BO_2^- via the intermediates BH_3OH^- , $\text{BH}_2(\text{OH})_2^-$ and $\text{BH}(\text{OH})_3^-$ [23,24]:

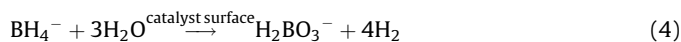


Subsequently, Co^{2+} ions chelated on Amberlite IR-120 resin were reduced with electrons liberated from borohydride anions to give metallic cobalt, shown like chalice in Fig. 3(e) and (f).



Furthermore, this flake-like cobalt has quite small feature, so that it was prone to being further oxidized to cobalt oxides like Co_2O_3 , Co_3O_4 and CoO . Additionally, side reactions, such as

disproportionation reaction of BH_4^- anions with water, on catalyst surface might take place simultaneously as well [23,24]:



As a result, various boric compounds and cobalt species might appear conjointly in Co/IR-120.

Results of TGA analyses on both Amberlite IR-120 resins (curve a) and Co/IR-120 catalysts (curve b) are displayed in Fig. 7. The observed decomposition process of IR-120 resin as temperature was raised from 30 °C to 900 °C could be divided into three stages: (1) firstly evaporation of crystallized water entrapped on IR-120 resin, (2) secondly by decomposition of active groups on the IR-120 resin and (3) finally by combustion of polymer matrices. Generally speaking, our TGA examination on the IR-120 resin is consistent

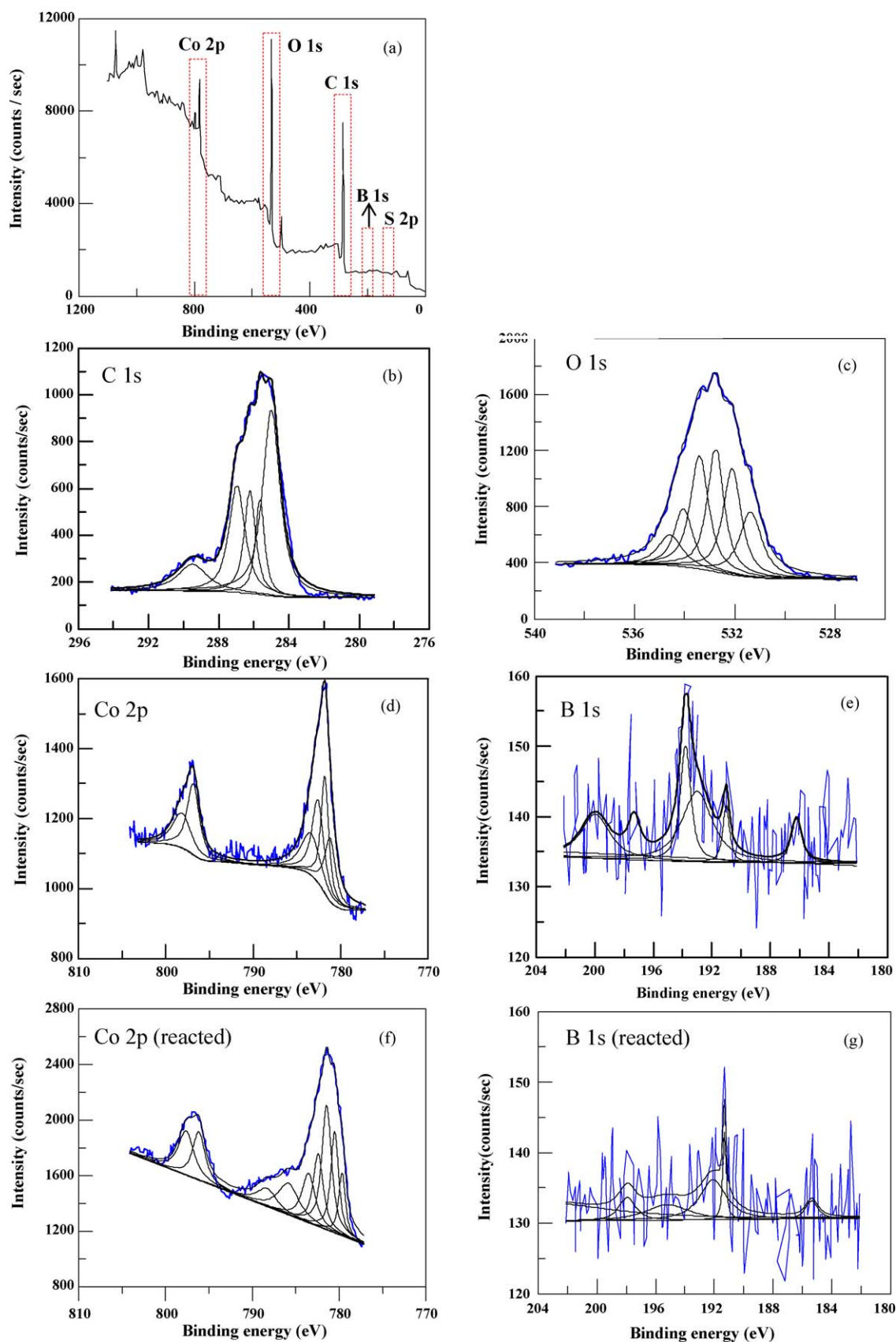


Fig. 6. XPS wide scan, C 1s, O 1s, Co 2p and B 1s core-level spectra of Co/IR-120 catalysts (a–e), and Co 2p and B 1s core-level spectra of used Co/IR-120 catalysts (f and g).

Table 2

Surface atomic compositions and possible dominative bonds in Co/IR-120 catalysts revealed by XPS analysis.

Elements	Conc. (at%)	Binding energy (eV)	Possible bonds
C 1s	65.0	285.0	C–C, C–H
		285.6	CO/Co
		286.2	C*–S and C*–O on polymer
		286.5	C graphite
		289.5	CO ₃ ^{2–}
O 1s	29.8	531.4	Co ₃ O ₄
		532.1	–C(O*)O– on polymer; –SO ₃ H on benzenesulfonyl
		532.9	B ₂ O ₃
		533.4	H ₃ BO ₃ ; B ₂ O ₃
		534.0	–C(O)O*– on polymer
		534.6	–C(O)O*– on phthlate
Co 2p	4.3	781.2	CoO; Co(OH) ₂ ; Co ₂ O ₃
		781.9	Co(OH) ₂
		782.6	Co ₃ O ₄
		783.2	Co(OH) ₂
		796.8	CoO; Co ₂ O ₃
		798.2	Co(OH) ₂
B 1s	0.8	186.2	B
		191.0	BN
		193.0	H ₃ BO ₃ ; B ₂ O ₃
		193.9	H ₃ BO ₃ ; B ₂ O ₃
S 2p	0.1	–	–

with a previous report under oxidation conditions [25]. The pyrolysis temperature of Amberlite IR-120 was raised apparently after resin surface loaded with cobalt, i.e. curve b of Fig. 7, which might be owing to the existence of cobalt that could shield surface of Amberlite IR-120 resin beads. Furthermore, the residual weight of Co/IR-120 catalyst remained nearly constant during the interval from 600 °C to 900 °C, indicating that cobalt accounted for approximately 30 wt% of Co/IR-120 catalysts.

3.2. Hydrogen generation

Factors influencing the catalytic performance of Co/IR-120 catalysts on hydrogen generation, for example, temperature and NaBH₄ loadings, were studied and discussed in this section. In addition, pH value of solution has also a profound influence on the hydrolysis of NaBH₄ especially in acidic environment [26]. Hence, in this work, alkaline condition was employed to preserve NaBH₄ from unwanted hydrolysis. Consequently, effect of NaOH concentration to hydrogen generation volume and rate was studied as well.

3.2.1. Hydrogen generation using pristine IR-120

The supports used in this study, IR-120 resin beads, are ion-exchange resin in acidic form and might lead to small production of hydrogen due to the low pH value near 3.1, when IR-120 resin beads are dispersed in water. In previous work [22], catalytic effects of pristine IR-120 resin beads were studied on hydrolysis of NaBH₄. Considerably, only a minute amount of hydrogen was generated, compared to that when Co/IR-120 catalysts were used. Therefore, catalytic effect of original IR-120 resin beans on hydrogen generation is negligible in this work.

Table 3

Contents of cobalt and boron on IR-120 resin beads and Co/IR-120 catalyst revealed by ICP analysis.

	Co (mg L ^{–1})	B (mg L ^{–1})
IR-120 resin beads	ND	0.8
Fresh Co/IR-120 catalyst	2855.7	35.2

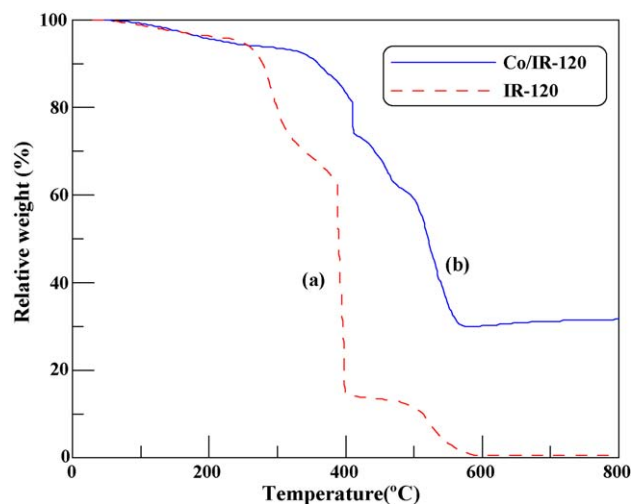


Fig. 7. TGA curves of (a) Amberlite IR-120 and (b) Co/IR-120 catalyst.

3.2.2. Effect of NaBH₄ concentration

Effect of NaBH₄ concentration, i.e. 1 wt%, 5 wt%, 10 wt%, 15 wt% and 25 wt%, in the presence of 1 wt% NaOH and 500 mg of Co/IR-120 catalyst on H₂ generation rate using water-displacement method at 25 °C is presented in Fig. 8. The amount of hydrogen generated is almost linearly proportional to the reaction time for all concentration of reactants studied, revealing the constant generation rate of hydrogen and stable catalytic activity of the catalysts. Furthermore, the linear relationship between amount of hydrogen generated and reaction time indicates that such a NaBH₄ hydrolysis reaction is of the zeroth order.

As NaBH₄ concentration increased from 1 wt% to 5 wt%, an apparent increase in H₂ generation rate from 23.3 mL min^{–1} g^{–1} to 53.1 mL min^{–1} g^{–1} was observed. It has to be mentioned that all weights of catalyst used and presented in this work were based on the bulk weight of Co/IR-120 catalyst. However, with a further increase in NaBH₄ concentration from 5 wt% to 25 wt%, the rate of hydrogen production was reduced to 26.5 mL min^{–1} g^{–1}. That is, 5 wt% of NaBH₄ solution with 1 wt% of NaOH in the presence of catalysts gives the highest production rate of hydrogen at 25 °C.

Similar results were reported by Ye et al. [17], who, utilizing a catalyst of Co supported on γ-Al₂O₃, found out 5 wt% NaBH₄ as an optimal concentration in H₂ generation. Amendola et al. [27] attributed it to the increase of viscosity in NaBH₄ solution for the

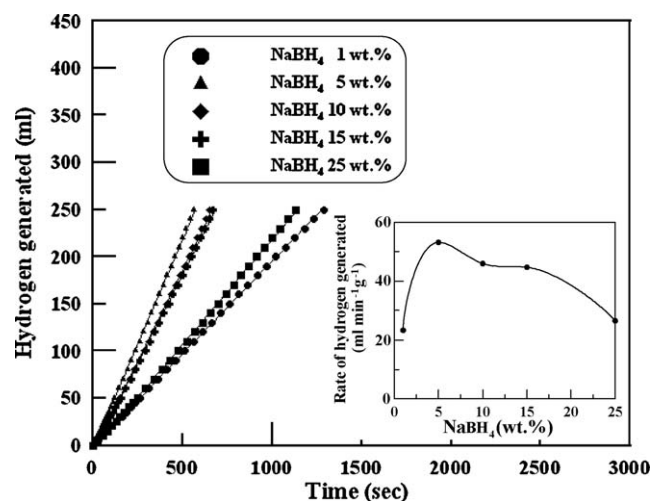


Fig. 8. Effect of NaBH₄ concentration on volume of hydrogen generated as a function of time in the presence of 1 wt% NaOH and 500 mg of Co/IR-120 catalysts at 25 °C.

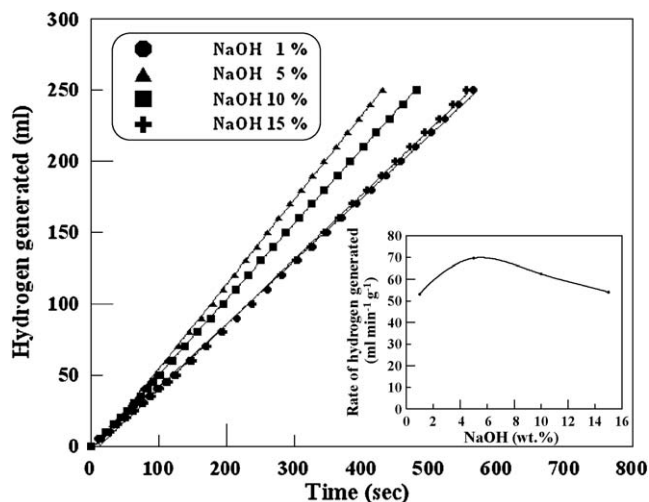


Fig. 9. Effect of NaOH concentration on volume of hydrogen generated as a function of time in 5 wt% NaBH_4 solution in the presence of 500 mg Co/IR-120 catalysts at 25 °C.

reduced rate of NaBH_4 hydrolysis with an excessive increase in NaBH_4 concentration. Furthermore, Suda et al. [28] pointed out that the hydrolyzed product of NaBH_4 is mainly sodium metaborate, NaBO_2 , which has a relatively smaller aqueous solubility, approximately 29 g/L, at 25 °C, compared with the higher aqueous solubility of NaBH_4 near 55 g/L at 25 °C. Such a lower aqueous solubility of NaBO_2 will result in precipitation of $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$, which interferes in mass transfer between NaBH_4 molecules and Co/IR-120 catalysts or wraps the catalysts to cover up active sites on the surface of catalysts to prevent NaBH_4 molecules from hydrolysis over active sites. In addition, the precipitated NaBO_2 will possibly contaminate the catalyst. Consequently, when NaBH_4 concentration increases over 5 wt%, generation rate of H_2 will drop apparently.

3.2.3. Effect of NaOH concentration

In order to prevent NaBH_4 from uncontrolled self-hydrolysis, NaBH_4 solution is generally maintained under high alkaline conditions by adopting NaOH as a stabilizer. Nevertheless, pH value and concentrations of alkaline solution are also known to influence the rate of hydrogen generation. Fig. 9 presents the effect of NaOH concentration, i.e. 1 wt%, 5 wt%, 10 wt%, and 15 wt%, on H_2 production rate at 25 °C in 5 wt% NaBH_4 solution added with 500 mg of Co/IR-120 catalysts using the water-displacement method. Similar to effect of NaBH_4 concentration on H_2 generation rate, measured hydrogen generation rate rose from 53.1 $\text{mL min}^{-1} \text{g}^{-1}$ to 69.7 $\text{mL min}^{-1} \text{g}^{-1}$ with NaOH concentration increasing from 1 wt% to 5 wt%. However, with a further increase in NaOH concentration, the generation rate of hydrogen was gradually reduced.

In regard to the effect of NaOH concentration, the hydrolysis mechanism of NaBH_4 differs on utilization of different catalysts. Jeong et al. [18] reported the usage of Co-B catalyst for hydrogen generation from NaBH_4 hydrolysis, in which H_2 production rate increased with increasing NaOH concentration. Similarly, an optimum concentration of NaOH at 10 wt% on H_2 generation rate was reported by Ye et al. [17]. Ye et al. [17] also pointed out that the rate of H_2 generation decreased apparently with a further increase in NaOH concentration beyond 10 wt%. However, no explanation to account for the observation was elucidated yet.

With our conjecture, it is possible that too much OH^- anions originated from an excessive amount of NaOH present in the NaBH_4 solution could significantly compete with the transfer of BH_4^- anions to catalytic surface, in which to some extent could be

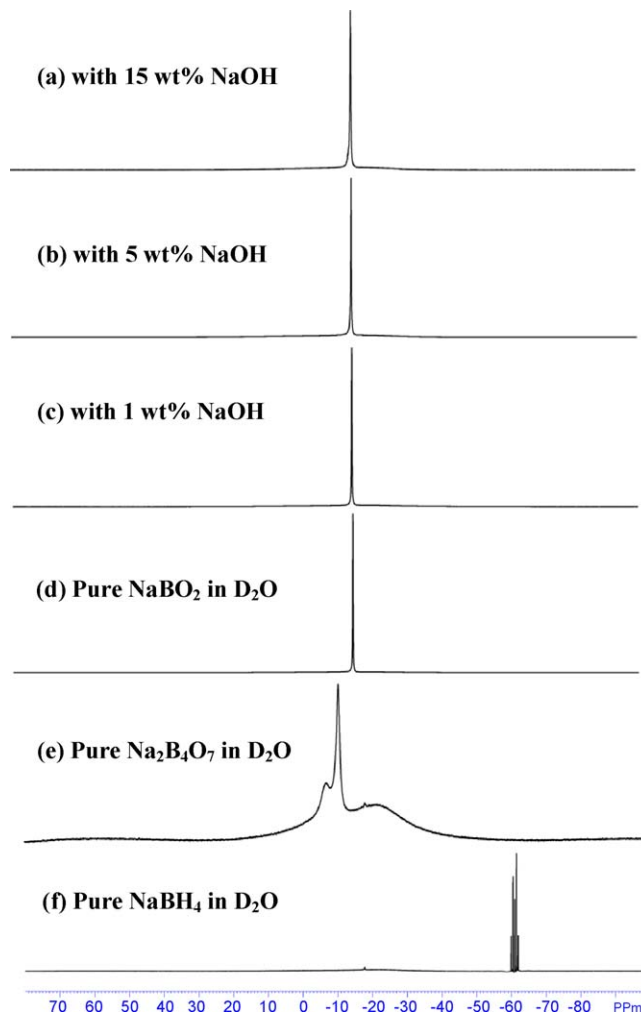


Fig. 10. ^{11}B NMR analyses of products remained after hydrolysis of 5 wt% NaBH_4 solutions containing 500 mg Co/IR-120 catalysts and (a) 15 wt% NaOH; (b) 5 wt% NaOH; and (c) 1 wt% NaOH at 25 °C. For comparison, (d), (e) and (f) represented ^{11}B NMR spectra of pure NaBO_2 , $\text{Na}_2\text{B}_4\text{O}_7$, and NaBH_4 in D_2O , respectively. A saturated solution of boron trifluoride diethyl etherate was used as an external reference.

occupied by OH^- anions rather than BH_4^- anions. That is, BH_4^- anions available on catalyst surface to generate hydrogen is reduced and so is the rate of hydrogen evolution. Further investigation is truly in need for clarifying mechanisms involved in the hydrolysis of NaBH_4 under various NaOH concentrations.

After completion of hydrogen generation of NaBH_4 solutions containing various NaOH concentrations in the presence of Co/IR-120 catalysts at 25 °C, products remained in spent NaBH_4 solutions were analyzed with ^{11}B NMR, as shown in Fig. 10. Comparing with chemical shifts of certain standard compounds relative to boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{C}_4\text{H}_{10}\text{O}$), for example, NaBO_2 at -14.5 ppm, $\text{Na}_2\text{B}_4\text{O}_7$ at -10 ppm and NaBH_4 at -60 ppm, products harvested from spent NaBH_4 solutions were identified to be NaBO_2 , consistent with the prediction on products corresponding to the hydrolysis reaction of NaBH_4 in Eq. (1). That is, hydrolysis products of NaBH_4 solution in this system were independent of NaOH concentration.

3.2.4. Effect of temperature

Influence of temperature on hydrogen generation rate in solutions containing 5 wt% NaBH_4 and 5 wt% NaOH was investigated at temperatures ranging from 25 °C to 50 °C (Fig. 11). As expected, increasing temperature gave rise to higher H_2 production rates. Furthermore, the linear relationship between amount of

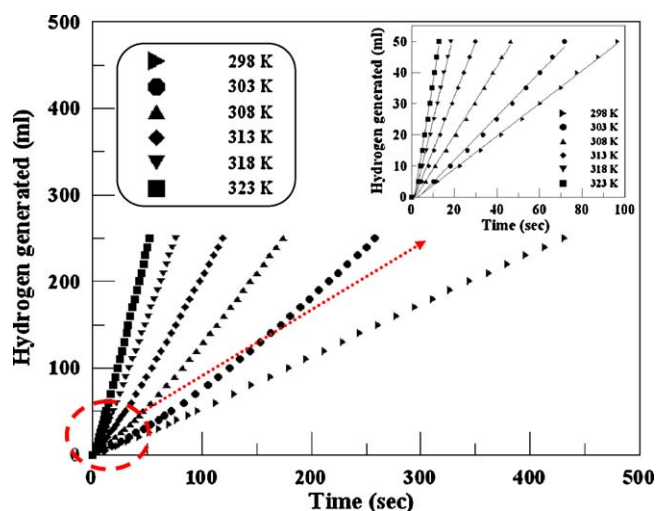


Fig. 11. Effect of temperature on volume of hydrogen generated as a function of time in 5 wt% NaBH₄ solution containing 5 wt% NaOH and 500 mg Co/IR-120 catalysts.

hydrogen generated and reaction time at each temperature studied was again observed, demonstrating that such a NaBH₄ hydrolysis reaction is of the zeroth order at temperatures ranging from 25 °C to 50 °C.

The reaction rate of the zeroth-order hydrolysis of NaBH₄ using Co/IR-120 catalysts can be represented as follows [17]:

$$r = k_{rxn} = k_0 \cdot \exp\left(\frac{-E_A}{RT}\right) \quad (6)$$

where r is the reaction rate (mL min⁻¹ g⁻¹) of NaBH₄ hydrolysis, k_0 the reaction constant (mol min⁻¹ g⁻¹), E_A the activation energy of the reaction (kJ mol⁻¹), R the universal gas constant and T is the reaction temperature.

With the Arrhenius plot of $\ln r$ vs. $1/T$ (Fig. 12), activation energy is estimated at 66.67 kJ mol⁻¹, comparable to 57.9 kJ mol⁻¹, 64.97 kJ mol⁻¹ and 44.47/54.89 kJ mol⁻¹ of activation energies obtained by Ye et al. [17], Jeong et al. [18] and Krishnan et al. [21], respectively, on usage of Co related catalysts. The activation energy obtained in this work is smaller than those with catalysts of pure metals and alloys, e.g. 75 kJ mol⁻¹ on cobalt, 71 kJ mol⁻¹ on nickel [27].

Compared with Co-based catalysts found in the literature [17], performance of Co/IR-120 catalysts in H₂ production rate from

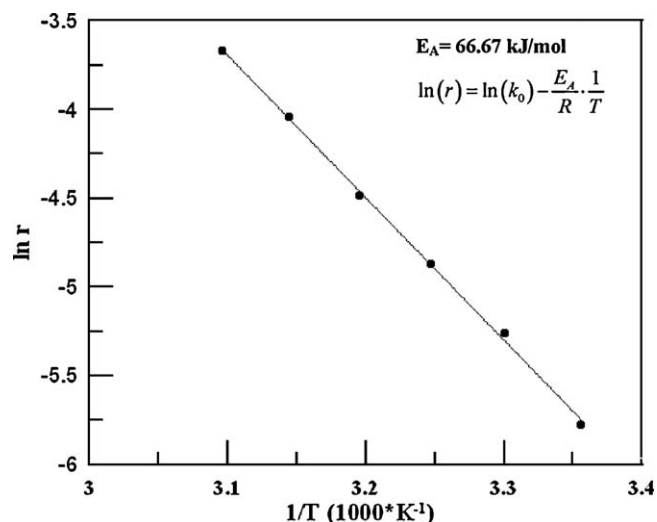


Fig. 12. Arrhenius plot obtained from the data shown in Fig. 11 for the hydrogen generation reaction using a Co/IR-120 catalyst.

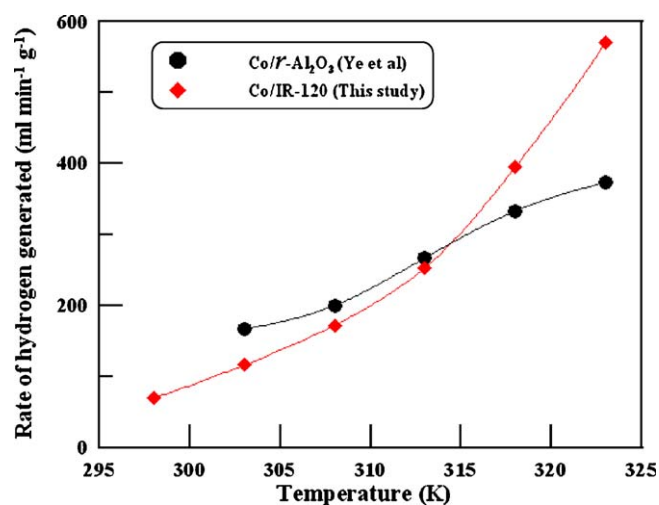


Fig. 13. Comparison of H₂ production rate at different temperatures of this work and those in Ref. [17]. In this work, 5 wt% NaBH₄ solution containing 5 wt% NaOH and 500 mg Co/IR-120 catalysts was used.

hydrolysis of NaBH₄ solution is superior at a higher temperature. As shown in Fig. 13, Co/IR-120 catalyst shows an improved rate of hydrogen generation at 45 °C and 50 °C, compared to that with cobalt catalysts supported on γ-Al₂O₃ [17].

3.2.5. Effect of Co/IR-120 catalyst on runoff behavior of NaBH₄ hydrolysis reaction

In order to understand the effect of Co/IR-120 catalyst on runoff behavior of NaBH₄ hydrolysis reaction on solution temperature and H₂ production rate, H₂ generation was carried out without temperature control in 100 mL of 5 wt% NaBH₄ solution containing 5 wt% NaOH and 200 mg Co/IR-120 catalysts using a continuous mass flowmeter (MFM). Fig. 14 clearly indicates that steadily stable hydrogen evolution rate could be reached approximately at around 200 mL min⁻¹ g⁻¹ after 60 min from onset of hydrolysis reaction. Temperature in the solution was around 35 °C with a variation less than 3 °C during the whole course of runoff test. That is to say, assuming a standard PEMFC operating at around 0.7 V and according to the calculation [14], supply rate of hydrogen near 200 mL min⁻¹ g⁻¹ to the PEMFC device could generate about 10 W of power per gram of Co/IR-120 catalyst at 35 °C. It is also noted that although temperature was not robustly controlled, still, no significant runoff on solution temperature was observed. Hence,

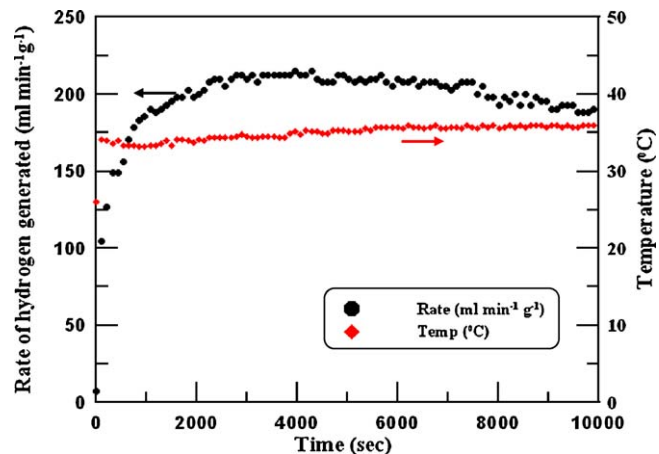


Fig. 14. Variation of H₂ production rate and solution temperature in 100 mL of 5 wt% NaBH₄ solution containing 5 wt% NaOH solution and 200 mg of Co/IR-120 catalysts without temperature regulated on the system.

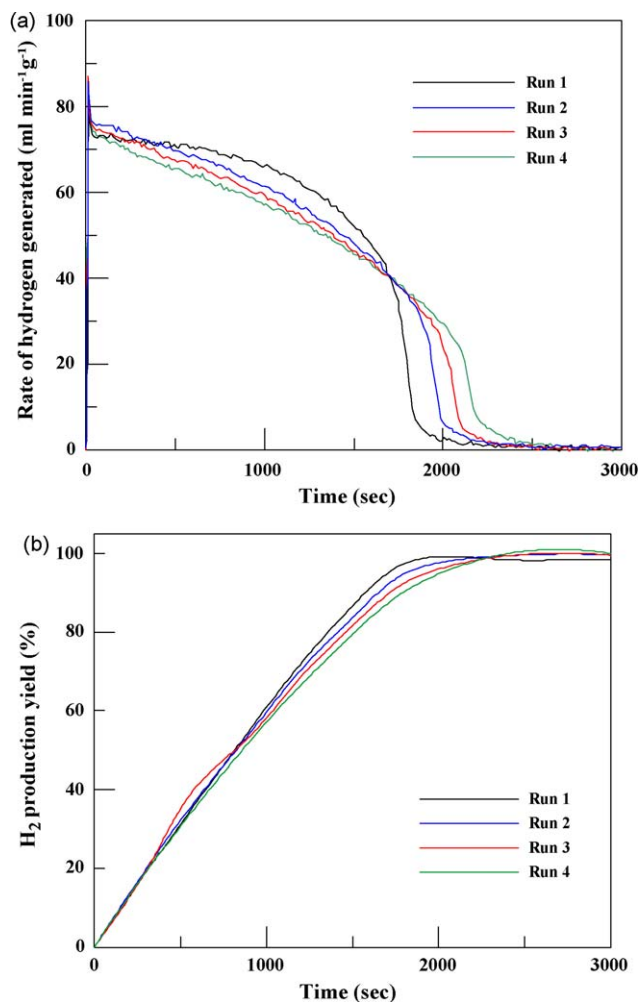


Fig. 15. Durability test of catalysts on (a) rate of hydrogen generation and (b) hydrogen production yield in 15 mL of 5 wt% NaBH_4 solution containing 5 wt% NaOH and 1 g of Co/IR-120 catalysts at 25 °C.

H_2 generation from the hydrolysis of NaBH_4 in the presence of Co/IR-120 catalyst can be maintained relatively stable.

3.2.6. Durability test of Co/IR-120 catalyst and characterization of used Co/IR-120 catalyst

Durability of Co/IR-120 catalyst was tested as well by repeating the same catalyzed hydrolysis experiment four times using the same batch of catalyst. After each run, the catalyst was collected with magnets and washed thoroughly with deionized water on filter paper. Fig. 15 shows the production rate and yield of hydrogen as a function of time in 15 mL of 5 wt% NaBH_4 solution using 5 wt% NaOH and 1 g of Co/IR-120 catalyst at 25 °C with a continuous mass flowmeter (MFM). During the hydrogen production process, the production rate of hydrogen fell gradually from initially ca. 75 $\text{mL min}^{-1} \text{g}^{-1}$ to ca. 40 $\text{mL min}^{-1} \text{g}^{-1}$, followed by a sharp halt owing to almost complete hydrolysis of NaBH_4 . The curves of H_2 production yield did not vary significantly in all four runs, which also clearly indicated almost 100% conversion of NaBH_4 could be reached. With 1 g of Co/IR-120 catalyst employed, the whole course of hydrogen evolution lasted for 30–35 min.

The surface chemistry of used Co/IR-120 catalyst was also examined by the XPS again. The atomic ratio of cobalt to boron (Co/B ratio) was about 66. The possible bonds of cobalt and boron on used Co/IR-120 did not change significantly. Namely, cobalt appeared mostly in oxidized forms on used Co/IR-120 catalyst. Notably, CoB or Co_2B was still absent on used catalysts. Although

Krishnan et al. [16] proposed that Co_3O_4 could be transformed to CoB during the hydrolysis experiment to account for the unique H_2 generation profile of Co containing oxides, such transformation in cobalt was not observed in this work. More works to tackle down the mechanism on how cobalt oxide catalysts could assist the hydrolysis of borohydride solutions should be warranted. Finally, results of this work implied that stable supply of hydrogen could be made possible from hydrolysis of sodium borohydride solution by using proper amount of Co/IR-120 catalysts under suitable conditions without temperature runoff.

4. Conclusion

Stable and cost-effective Co/IR-120 catalysts having high remnant magnetism suitable for hydrogen generation from hydrolysis reaction of alkaline NaBH_4 solution were synthesized using a wet-chemical reduction method. Sodium metaborate was confirmed with NMR analysis as the main solid hydrolyzed product of borohydride solutions. Briefly, the Co/IR-120 catalysts were acquired as cobalt ions chelated on Amberlite IR-120 resin support with ion-exchange were reduced directly with borohydride solution. The surface chemistry of these Co/IR-120 catalysts, made from the reduction of chelated cobalt ions on polymer resin by borohydride solution, was mainly cobalt oxides, not cobalt borides (Co_2B) found on catalysts synthesized from direct reduction of cobalt ions by borohydride anions. Co loading on Co/IR-120 catalyst was near 30 wt%.

Such a wet-chemical method provides a fast and easy way to produce Co/IR-120 catalysts in large quantity. Intrinsic ferromagnetism of Co/IR-120 catalysts really gives an advantage and a convenient way to recycle and reuse of the catalysts from spent NaBH_4 system after hydrogen production, and renders a robust controllability in hydrogen generation process. For example, with permanent magnets it becomes simple to separate the catalysts from NaBH_4 solutions to stop the hydrogen production, when hydrogen is no more required in in-line applications.

As Co/IR-120 catalysts were used for H_2 generation from hydrolysis of alkaline borohydride solutions, a hydrogen production rate from 53 $\text{mL min}^{-1} \text{g}^{-1}$ at 25 °C to 571 $\text{mL min}^{-1} \text{g}^{-1}$ at 50 °C was achieved in solution having 5 wt% of NaBH_4 and 5 wt% NaOH in the presence of 500 mg of Co/IR-120 catalyst. In general, stable hydrogen generation rate near 200 $\text{mL min}^{-1} \text{g}^{-1}$ without run-off of temperature, which fell within the 33 °C and 36 °C, was achieved in 100 mL of 5 wt% NaBH_4 solution containing 5 wt% NaOH solution and 200 mg of Co/IR-120 catalyst. Rates of H_2 generation increase with increasing temperatures. The activation energy of NaBH_4 hydrolysis reaction was found at 66.67 kJ mol^{-1} , which was comparable with others reported in the open literatures.

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References

- [1] R.J. Farrauto, Appl. Catal. B: Environ. 56 (2005) 3–7.
- [2] J.J. Baschuk, X. Li, Int. J. Energy Res. 25 (2001) 695–713.
- [3] Y. Matsumura, H. Ishibe, Appl. Catal. B: Environ. 86 (2009) 114–120.
- [4] C.Y. Yu, D.W. Lee, S.J. Park, K.Y. Lee, K.H. Lee, Appl. Catal. B: Environ. 86 (2009) 121–126.
- [5] W.L.S. Faria, L.C. Dieguez, M. Schmal, Appl. Catal. B: Environ. 85 (2008) 77–85.
- [6] C. Wu, P.T. Williams, Appl. Catal. B: Environ. 87 (2009) 152–161.
- [7] Z.P. Li, B.H. Liu, K. Arai, N. Morigazaki, S. Suda, J. Alloys Compd. 356–357 (2003) 469–474.
- [8] B. Tumas, 2007 Annual Merit Review Proceedings—Hydrogen Storage, May 2007.

- [9] Z.P. Li, N. Morigazaki, B.H. Liu, S. Suda, J. Alloys Compd. 349 (2003) 232–236.
- [10] Y. Kojima, T. Haga, Int. J. Hydrogen Energy 29 (2003) 993–999.
- [11] C.H. Hale, H. Sharifian, US Patent 4,931,154 (1990).
- [12] C.L. Hsueh, C.H. Liu, B.-H. Chen, C.Y. Chen, Y.C. Kuo, K.J. Hwang, J.R. Ku, Int. J. Hydrogen Energy 34 (2009) 1717–1725.
- [13] M.M. Krevoy, R.W. Jacobson, Ventron Alembic 15 (1979) 2–3.
- [14] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, M. Binder, J. Power Sources 85 (2000) 186–189.
- [15] D. Hua, Y. Hanxi, A. Xinping, C. Chuansin, Int. J. Hydrogen Energy 29 (2003) 1095–1100.
- [16] P. Krishnan, K.L. Hsueh, S.D. Yim, Appl. Catal. B: Environ. 77 (2007) 206–214.
- [17] W. Ye, H. Zhang, D. Xu, L. Ma, B. Yi, J. Power Sources 164 (2007) 544–549.
- [18] S.U. Jeong, R.K. Kim, E.A. Cho, H.J. Kim, S.W. Nam, I.H. Oh, S.A. Hong, S.H. Kim, J. Power Sources 144 (2005) 129–134.
- [19] J. Zhao, H. Ma, J. Chen, Int. J. Hydrogen Energy 32 (2007) 4711–4716.
- [20] H.I. Schlesinger, H.C. Brown, A.E. Finholt, J.R. Gilbreath, H.R. Hoekstra, E.K. Hyde, J. Am. Chem. Soc. 75 (1953) 215–219.
- [21] P. Krishnan, S.G. Advani, A.J. Prasad, Appl. Catal. B: Environ. 86 (2009) 137–144.
- [22] C.L. Hsueh, C.Y. Chen, J.R. Ku, S.F. Tsai, Y.Y. Hsu, F.H. Tsau, M.S. Jeng, J. Power Sources 177 (2009) 492–495.
- [23] G.O. Mallory, J.B. Hajdu, Electroless Plating: Fundamentals and Applications, American Electroplaters and Surface Finishers Society, Orlando, FL, 1990.
- [24] K.A. Holbrook, P.J. Twist, J. Chem. Soc. A (1971) 890–894.
- [25] R.S. Juan, T.S. Lee, J. Hazard. Mater. B92 (2002) 301–314.
- [26] C.M. Kaufman, B. Sen, J. Chem. Soc., Dalton Trans. (1995) 307–313.
- [27] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, M. Binder, Int. J. Hydrogen Energy 25 (2000) 969–975.
- [28] B.H. Liu, Z.P. Li, S. Suda, J. Alloys Compd. 469 (2009) 493–499.